Deliverable report

Deliverable no./title: D4.3 Production of 3D printing filament
Lead beneficiary: CTB
Nature of deliverable: Report
Dissemination level: Public
Due date: 30.12.2022

Grant Agreement number: 820477
Project acronym: CREAToR
Project title: Collection of raw materials, Removal of flAme reTardants and Reuse of secondary raw materials
Funding scheme: H2020-SC5-2018-2019-2020
Coordinator: FRAUNHOFER GESELLSCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V.
Project Website: www.creatorproject.eu

Document history and contribution of the partners

Table 1: Version management

Version nr	Reviser	Content
1	CTB	Report description
2	ICT	Revision 1
3	CTB	Revision 2
4	ICT	Submission

Table 2: Partners' contribution to the deliverable

Partner	Short name	Role in the WP	Contribution to the deliverable
Centexbel	CTB	Participant WP4	Production of 3D print filament and
Maier S. Coop.	MAI	WP Leader	Managing WP partners' work and info, providing feedback on material quality
Coolrec BV	CLR	Participant WP4	Providing raw materials
Cyclefibre S.L.	CYC	Participant WP4	Evaluation printing of filaments
ITRB Group	ITB	Participant WP4	Evaluation printing of filaments
Fraunhofer ICT	ICT	Coordinator	Revision and submission

Abbreviations

ABS	Acrylonitrile butadiene styrene
AM	Additive manufacturing
C&DW	Construction and demolition waste
DLP	Digital light processing
DSC	Differential scanning calorimetry
EEE	Electrical and electronic equipment
FFF	Fused filament fabrication
FDM	Fused deposition modelling
HBCD	Hexabromocyclododecane
MFR	Melt flow rate
PA	Polyamide
PET	Polyethylene terephthalate
PLA	Polylactic acid
PU	Polyurethane
RABS	Recycled ABS
SLA	Stereolithography
SLS	Selective laser sintering
Tg	Glass transition temperature
TGA	Thermal gravimetric analysis
TPU	Thermoplastic polyurethane
WEEE	Waste electrical and electronic equipment

TABLE OF CONTENTS

1 INTRODUCTION

The EU-funded project CREAToR focusses on process development and demonstration (to TRL 5) to remove hazardous, already banned bromine-containing flame-retardants from waste streams using continuous purification technologies (supercritical CO_2 and cost-effective solvent-based processes using natural deep eutectic solvents (NADES)) in twin-screw extruders. CREAToR covers the whole value chain, starting from collecting thermoplastic waste streams from construction and demolition waste (C&DW) and from waste electrical and electronic equipment (WEEE). Recyclers and sorters of both industries are part of the CREAToR consortium. The project is implementing ways to collect secondary raw materials, identify the presence of hazardous flame retardants, remove these contaminants and finally reuse the materials. As case studies the materials will be reused as valuable secondary raw materials for new building and construction (B&C) insulation panels (creating a circular economy), for automotive interior application, and for producing 3D printed parts for aerospace applications. The end user partners for each sector are also part of the CREAToR consortium. To further increase the economic feasibility of the approach, an optimised logistic concept and a harmonised material quality classification scheme is being developed and applied.

The use of sustainable materials is one of the current demands in the additive manufacturing sector. This deliverable D4.3 Production of 3D printing filament (CTB, M42) describes the production of a 3D print filament out of recycled ABS. The 3D print filament will be used to print different aerospace applications.

The focus of the study is the production of a good quality 3D print filament which can be used on a FDM (fused depositoin modelling) 3D printer.

2 MATERIALS AND METHODOLOGIES

2.1 MATERIAL: RECYCLED ABS

As a starting material, recycled ABS from WEEE and fridges supplied by the partner Coolrec was used. The materials were shredded and sorted using density baths. An additional metal decontamination step was performed. After sorting and separation, the flakes were further compounded into pellets which are used as raw materials during the filament extrusion (Figure 1).

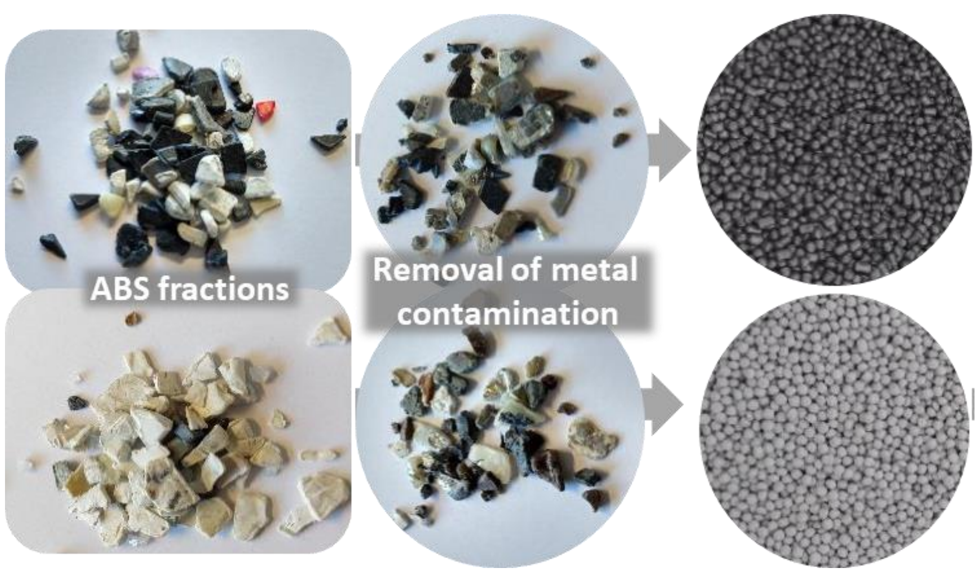

Figure 1: ABS waste streams

2.2 3D PRINT PRODUCTION TECHNOLOGIES

Additive manufacturing (AM), also known as 3D-printing, is an innovative technique, the global importance of which cannot be underestimated. The 2019 report from Wohlers – recognised as one of the preeminent 3D printer experts in the world – forecasts a $23.9 billion revenue growth in the 3D-printing industry by 2022, and $35.6 billion by 2024.[1]

3D printing is already performed with a variety of materials: metals, polymers, ceramics and concrete. Metal 3D-printing is predominantly used for advanced applications in the aerospace industry because traditional processes are more time consuming and costly. Ceramics are mainly used in 3D-printed scaffolds, while concrete is the main material employed in the additive manufacturing of buildings. Polymers are considered as the most common materials in the 3D printing industry due to their diversity and ease of adaption to different 3D printing processes.[2]

3D-printing with polymers seems the most obvious choice. To process polymers, various 3D printing techniques are available, which can be subdivided as follows: techniques for thermoplastic polymers, which are polymers that can be remelted and reshaped, and techniques for thermosets, which are polymers that remain in a solid state after curing (Figure 2).

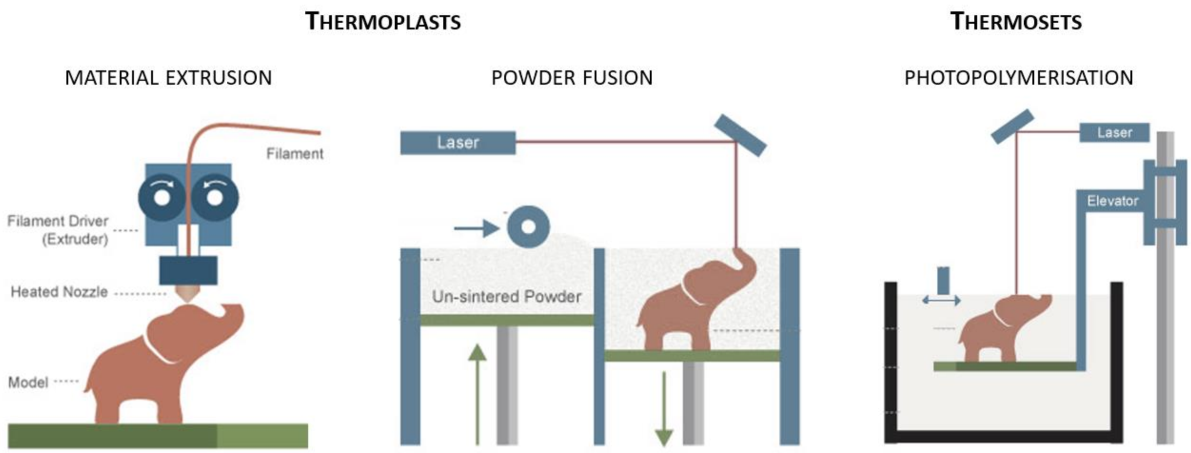

Figure 2: Main polymer-based 3D-printing techniques

Typical techniques used for thermoplasts are material extrusion and powder fusion. In material extrusion, the material is selectively dispensed through a nozzle. Fused filament fabrication (FFF) and 3D dispensing fall into this category. In powder fusion techniques, regions of a polymer powder bed are fused through a laser beam (selective laser sintering) or a liquid bonding agent (binder jetting)

3D-printing techniques for thermosets are typically based on a photopolymerisation process. In such a process, a liquid photopolymer in a vat is selectively cured by light-activated polymerisation. Many of the lithography-based AM approaches, like stereolithography (SLA) and digital light processing (DLP) can be grouped into this category. The main techniques will be briefly described.

---

[1] Wohlers, T. T.; Campbell, I.; Diegel, O.; Huff, R.; Kowen, J., Wohlers Report 2019: 3D printing and additive manufacturing state of the industry; Wohlers Associates Inc.: 2019

[2] Ngo, T.D; Kashani, A.; Imbalzano, G.; Nguyen, K.T.Q.; Hui, D. Additive manufacturing: A review of materials, methods, applications and challenges. Composites Part B. 2018, 143, pp. 172-196; DOI 10.1016/j.compositesb.2018.02.012

Fused filament fabrication or FFF is also known under the trademarked term of fused deposition modeling (FDM). FFF-based printers use a thermoplastic filament that is pushed through a heated extruder head (including one or more extrusion nozzles) using a drive wheel. The head can be driven both horizontally and vertically, creating one layer at a time before adjusting vertically to begin a new layer.

The polymeric materials used should be extrudable into filaments, and should be rigid enough to avoid buckling between the drive wheels, but flexible enough to be spooled and strong enough to avoid shearing due to pinching from the wheels. Despite these demands, numerous thermoplastic-based materials are available as filaments for FFF. The most common polymers are acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA). Other examples are polyamide (PA), polyurethane (TPU), polyethylene terephthalate (PET), etc. Many more materials and combinations are possible: the FFF technique offers significant freedom in material choice. Beside its low costs and its simple and open source machine structure, this is one of the main reasons that FFF is one of the most widespread AM methods. The following companies are just a few of the many producers of FFF printers: Ultimaker, RepRap, Makerbot Systems, Leapfrog, Prusa Printers. A fused filament fabrication (FFF) – Ultimaker S5 is used in this study (Figure 3).

Figure 3: Fused filament fabrication (FFF) – Ultimaker S5

Some of the more recent 3D-printers employ a screw-based extrusion system, making it possible to use standard polymer pellets instead of filaments. The use of pellets paves the way to a much broader range of materials, since the criteria for a filament as described above are not relevant anymore. If a polymer works to a certain extent with injection molding, then it will work with this technology.

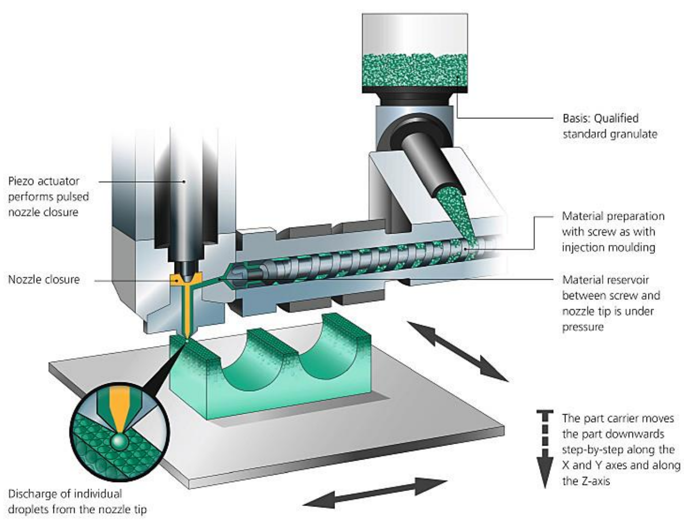

Figure 4: Arburg Plastic Freeformer with extrusion system

An example of a pellet 3D-printer is the Arburg Freeformer (Figure 4): first, the polymer granulate is melted in a cylinder unit, after which it is transported by a screw towards a nozzle tip. By use of a discharge unit and variable pressure, the melt is deposited onto a platform layer by layer as tiny droplets. Another 3D-printer starting directly from pellets instead is the Pollen AM. This printer is capable of printing with up to four different materials, and it is also capable of mixing two materials during the printing process. The two mentioned pellet printers are designed to manufacture small objects. However, there are also pellet 3D-printers on the market for the manufacturing of large-format objects. Examples of such large printers are the Titan Robotics Atlas, Colossus or the CFAM Prime.

2.3 Extrusion of 3D print monofilament

A pilot-line equipment can be used to convert the polymers into any type of textile yarns: yarns, monofilaments, tapes and bicomponent yarns. An extruder allows a large variety of polymer flow rates for pilot scale productions from 0.250 to ± 5 kg/hour. The low flow rates are especially important to process experimental products that are only available in very limited quantities. It also includes the possibility to extrude both thick (several mm) and thin (< 40 µm) filaments. The extrudate is cooled in a cooling water bath with a temperature range from 15 to 70 °C. The filaments can be drawn by means of four roller sets, each with an adjustable temperature and intermediate ovens allowing the process to take place in several steps to optimise both strength and stability. For the production of a 3D print filament no additional drawing steps are performed. The filaments are wound directly on a godet (Figure 5).

Figure 5 : Monofilament extrusion lines

2.3.1 Melt flow rate

The melt flow rate (MFR) gives an indication of the flowability of a plastic at a certain temperature and load. Granules of the compounds were used for the measurements. The MFR of the samples was determined at a temperature of 220 °C with a load weight of 10 kg (Figure 6).

Figure 6: MFR instrument

2.3.2 DSC ANALYSIS

Differential scanning calorimetry, or DSC, is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. In general, the temperature programme for a DSC analysis is designed so that the sample holder temperature increases linearly as a function of time (**Fehler! Verweisquelle konnte nicht gefunden werden.**).

When a material is heated, a chemical or physical reaction can occur which is linked to the absorption or release of heat. DSC equipment is able to measure these energy changes.

Figure 7: DSC instrument

2.3.3 TGA ANALYSIS

TGA is an analytical method that measures the changes in weight of a test sample during a heating process. A sample (5 à 10 mg) is placed on a fireproof tray. The tray is placed on a balance in an oven. A thermocouple is placed alongside the tray to log the temperature. The weight of the tray is measured as a function of the temperature in the oven or the residence time. The temperature typically rises to 900 °C. The oven can be flushed with pure nitrogen to prevent oxidation of the sample material. The result of the test is weight reduction due to decomposition or evaporation. The weight changes often indicate which materials decompose or evaporate. The temperatures that provoke these occurences are typical for certain components in a plastic matrix (**Fehler! Verweisquelle konnte nicht gefunden werden.**).

Figure 8: TGA instrument

3 Results

3.1 Production of a recycled ABS 3D print filament

Purified and granulated white and black ABS grades obtained from Coolrec were processed via yarn/filament extrusion equipment. Figure 9 shows the material flow which was involved in this step.

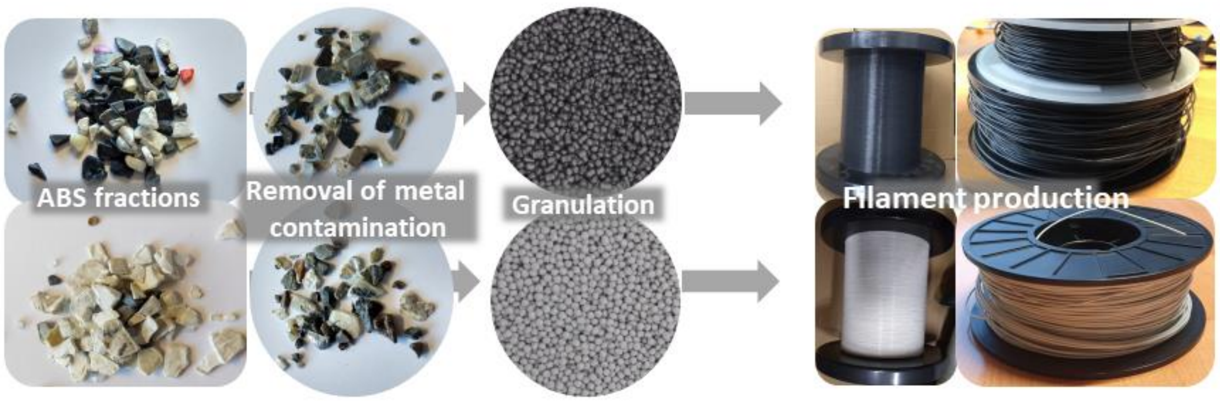

Figure 9: Pictures of the ABS fractions, containing metal contaminations, which were treated via melt filtration to obtain metal-free granules. The latter were used in yarn/filament extrusion equipment to obtain filaments of different diameters

For each type, physical characterisation tests such as MFR, DSC and TGA were performed on the granules prior to processing.

3.1.1 Melt Flow Rate

As can be seen in Table 3, the melt flow rate of the black recycled ABS is higher than the melt flow rate of the white recycled ABS. Both materials have a melt flow rate suitable for producing monofilaments.

Table 3: MFR results rABS

Sample No.	MFR in g/10 min
White r-ABS	23.70
Black r-ABS	36.50

3.1.2 DSC ANALYSIS

As ABS is an amorphuous material, no melting and crystallisation temperatures are noticed. A similar melting trajectory was measured for both materials (Figure 10).

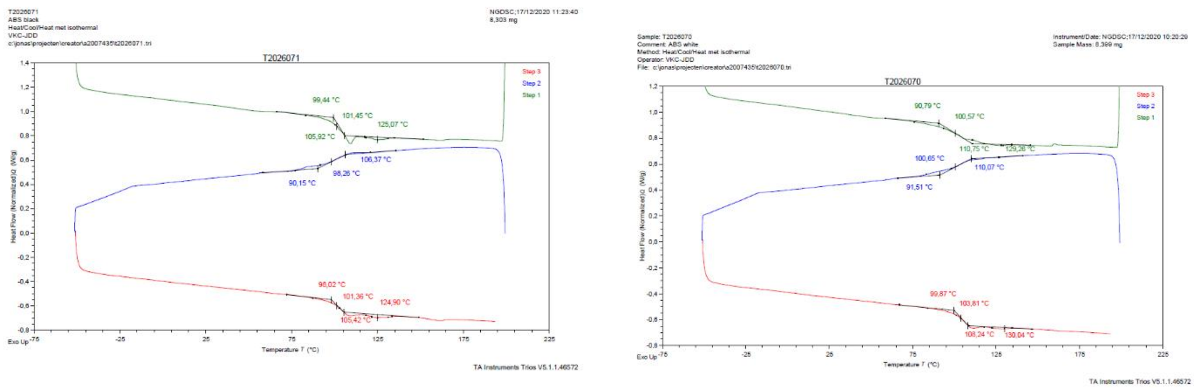

Figure 10: DSC curves: left black r-ABS, right white r-ABS

3.1.3 TGA ANALYSIS

No differences in degradation profile were detected between the recycled ABS samples. The material is stable up to temperatures of 300 °C, indicating that the extrusion of the monofilament samples can be safely performed (Figure 11).

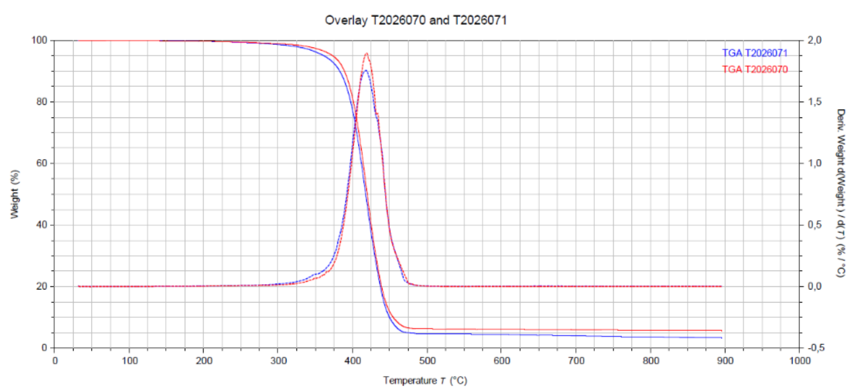

Figure 11: TGA curves: black r-ABS, and white r-ABS

3.1.4 MONOFILAMENT PRODUCTION

In a next step, filaments with a diameter of 0.18 mm and 1.75 mm were produced using the following extrusion settings (Table 4):

Table 4: settings monofilament extrusion

PARAMETER	VALUE
TEMP.PROFILE EXTRUDER (°C)	175-190-210-210°C
TEMP SPINPACK (°C)	210-210°C
TYPE SPINNERET	1 X 4 MM ROND
EXTRUDER PRESSURE (PSI)	652
EXTRUDER PRESSURE (BAR)	45,0
SPINPUMP PRESSURE (BAR)	3,6
SPINPUMP FLOW RATE (RPM)	11,4
TEMP. WATER BATH (°C)	25°C
DISTANCE WATER BATH (CM)	1,2 CM
WATER BATH CIRCULATION (Y/N)	Y
TAKE-UP ROLLS SPEED (M/MIN) - SET	5,6
TAKE-UP ROLLS SPEED (M/MIN) - MEASURED	5,5-5,7

In the case of the black ABS, both filaments could be produced successfully, although it should be mentioned that the finest filaments obtained (diameters of 0.175-0.180 mm; referred to as yarns) appeared very brittle, meaning that a new coil (bobbin) had to be installed as soon as filament rupture appeared. Also, hard impurities were noticed along the filament. This could be due to contaminants still present in the recycled material.

In the case of the white ABS, no stable process could be obtained during the production of the finest filaments. After 1 hour of trials, significant variations in the extruder pressure were observed and filament rupture was occurred frequently. Consequently, no significant quantities of the white thin filament could be produced. Dismantling of the equipment showed white sticky depositions on the spinning plate. These probably caused the pressure fluctuations and, as discussed with Coolrec, they most likely originate from the glues that are used during refrigerator production (Figure 12).

Figure 12: Contamination of spinning plate: cause of variations in extruder pressure

For the 1.75 mm filaments (referred to as filaments), variations were noticed in the filament diameter (Figure 13).

Figure 13: Standard 1,75 mm filament (left), first trial for very thin filament (right) --> no stable production process yet for the white ABS; better results with the black ABS.

The mechanical properties of the produced filaments were determined. Table 5 shows the results of the tensile tests performed on yarn and filament level.

On yarn-level, it seems that the black yarn is somewhat stiffer and stronger than the white yarn. On filament level, comparable mechanical properties are obtained for both types (i.e. black and white) ABS.

Table 5: Mechanical properties of the produced yarns and filaments.

	E-MOD (GPA)	TENACITY AT BREAK (N/TEX)	STRAIN AT BREAK (%)
WHITE YARN	**2,6** ± 0,2	**0,08** ± 0,005	**51** ± 5
BLACK YARN	**3,1** ± 0,2	**0,10** ± 0,008	**40** ± 1
WHITE FILAMENT	**2,0** ± 0,1	**0,04** ± 0,003	**3** ± 0,3
BLACK FILAMENT	**2,0** ± 0,01	**0,04** ± 0,000	**3** ± 0,1

In a second run, 1.75 mm and 2.85 mm thick filaments were produced using the same settings in larger amounts. The 1.75 mm filament was used by Cyclefiber to produce the demonstrator. The 2.85 mm filament was used for further characterisation. Figure 14 shows an overview of the results.

For both the recycled black filament and a commercial ABS filament (green), tensile bars were printed. The printing process showed that the use of recycled material resulted in a different processability. Unlike the commercial grade, it was not possible to print it on the standard glass plate, but rather an underground had to be used. As can be seen, the best results were obtained when a TPU underground was used, as bending of the edges was minimised in this case. The latter was very apparent when a textile underground was used.

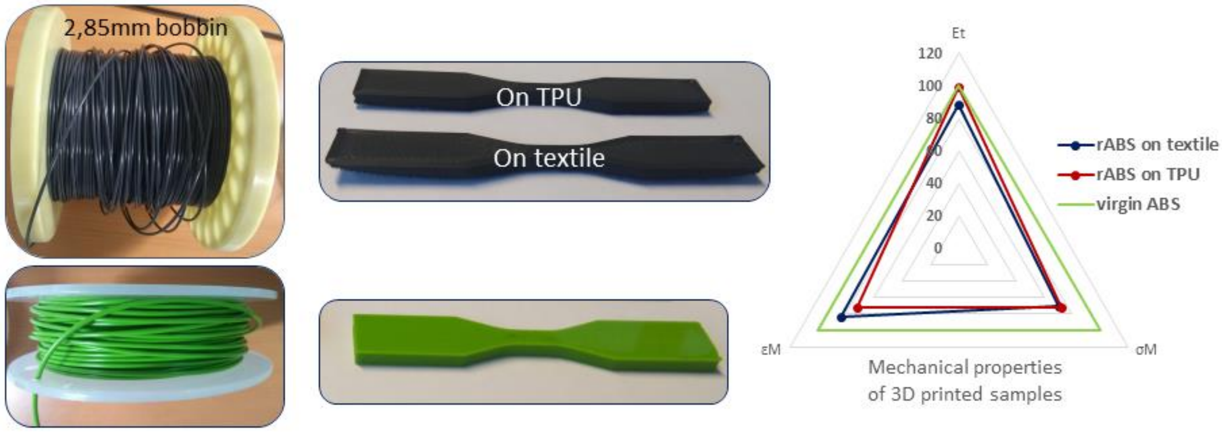

Figure 14: Picture of a bobbin with 2.85 mm recycled black filament and commercial green ABS filament, the 3D printed tensile bars and a comparison of their mechanical properties.

Mechanical analysis of the samples showed that a similar material stiffness was obtained for the commercial and recycled ABS, whereas the strength and elongation properties were lower for the rABS. These differences can probably be attributed to impurities, such as polyolefins, which are present in the recyclate.

3.1.4.1 DSC ANALYSIS

When comparing the DSC curves of the rABS and the virgin ABS it could be noticed that the Tg of the rABS was higher and two small melting peaks at 125 and 160 °C are detected (Figure 15).

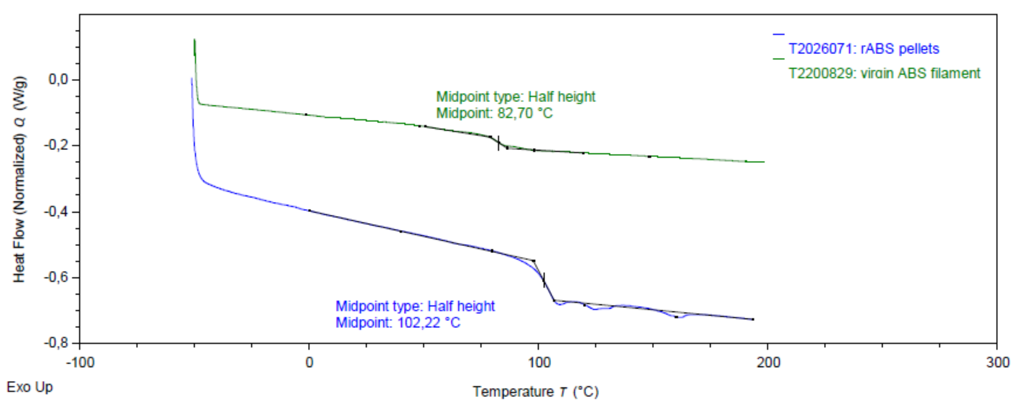

Figure 15: DSC curves: blue rABS, green virgin ABS

3.1.4.2 TGA ANALYSIS

A faster degradation of the rABS was noticed. The rABS also contains 3.3 % inorganic additives, as could be seen in the residue after heating (Figure 16).

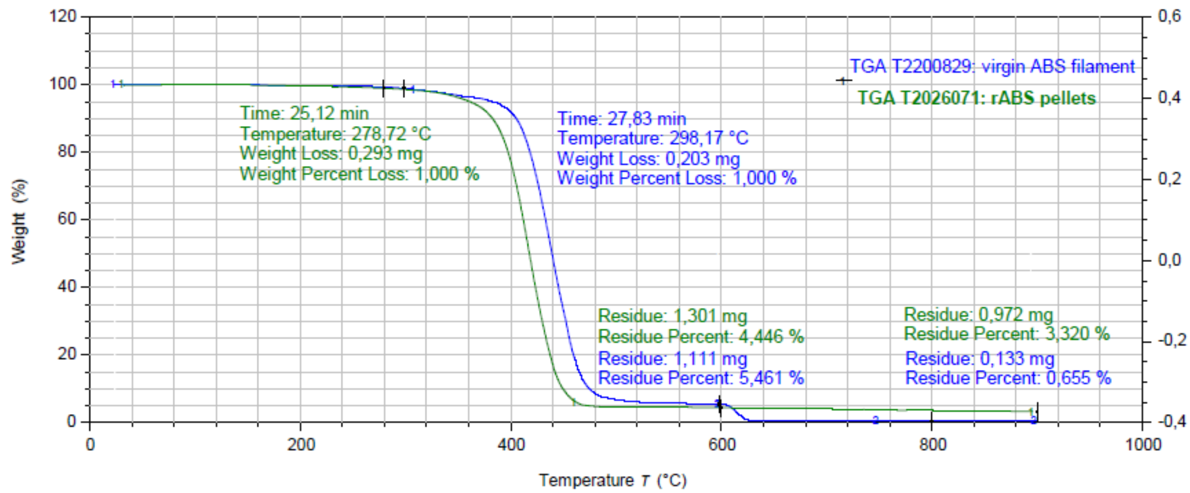

Figure 16: TGA curves: green rABS, blue virgin ABS

3.1.4.3 PROCESSING OF FR ADDITIVATED RECYCLED ABS-COOLREC MATERIALS

The white recycled fridge material from Coolrec was additivated with flame retardants by partner CIDAUT, with 5 and 15 % MDH (magnesium hydroxide). The processing of the filament was fluent. Again, white depositions occurred on the spinning plate after removal from the machine, but it could be cleaned by applying 2 burning cycles (Figure 17).

Larger amounts will still be produced for Cyclefiber for demonstrator production.

Figure 17: TGA White rABS filaments, additivated with 5 and 15% MAH.

4 CONCLUSION

Recycled ABS material was successfully used to produce 3D print filaments. The material properties were determined and a number of small-scale tests were performed, demonstrating the feasibility. In a second step larger quantities were produced and supplied to Cyclefiber in order to produce 3D-printed aerospace components made from the recycled filament, following the specifications required. The components will be evaluated in real operating conditions, and their performance will be compared with that of the parts currently manufactured using virgin material.